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Decomposition of NOx and PM emission in Diesel Exhaust by Electrochemical reactor withMultilayered Electrodes

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Abstract

NOx emissions are highly poisonous and reactive gas liberated excessively from diesel engines. This work attempts to decrease NOx emissions by developing electrochemical reactor. The electrochemical reactor consists of electrochemical cells placed inside it. The electrochemical cells are fabricated by YSZ as an electrolyte middle layer coated with NiO -YSZ as cathode layer and Ag-YSZ as anode layer. The electrochemical cells are tested with diesel exhaust in a single cylinder dieselengine. By passing the variable voltage to the electrochemical cell, it is observed that up to 80 % NOx reduction, 75% PM reduction and 75% HC reduction was achieved with electrochemical cell. Further by coating the BaO NOx storage material, NOx reduction was reduced to 85%, PM reduction up to 76% and HC reduction up to 80 % was achieved. NOx reduction was greater with electrochemical cell -2.The presence of NOx storage material causes more NOx decompositions in the cathode layers. NOx decomposition also increases the oxygen concentrations, which further oxidizes the HC and PM emissions.The increase in NO decomposition was due to the increase in the ionic conductivity of the YSZ substrate. NOx reduction by electrochemical cell is a cost effective method.

Keywords: Diesel, Biodiesel, Engine, Emission, Electrochemical

Introduction

Nitrogen oxide (NO and NO_2) are collectively referred as NOx. The oxidation of atmospheric nitrogen at higher temperature in combustion produces NOx emission. NOx emissions cause serious environmental and health problems. The increase in oxygen concentration, diesel engines produce higher NOx emissions [1].The total concentration of NOx emissions in diesel engine exhaust generally ranges from 100 to 1000 ppm. NOx emission causes serious problems for human beings, which leads to air way irritation, coughing, Asthma, inflammation and permanent lung damage. In environment NOx emissions causes acid rain and photochemical smog [2].Electro chemical NOx reduction is the better concept works well for the reduction of NOx during excess oxygen exhaust conditions [3-4]. The fig. 1shows the mechanism of Electrochemical cell. In this concept by varying the electric potential, NOx molecules are reduced to nitrogen gas (N_2) and oxygen ions (O^{2-}) at the cathode The oxygen in the cathode is ionically transferred over electrolyte and reaches the cathode to oxidize the PM deposited in the anode. The concept of Electrochemical NOx reduction was first reported by Pancharatnam et al [5] proposed decomposition of NOx using ion conducting materials in the cell using Y-ZrO_2 by applying high voltage. Later, Huggins et al [6] proposed the electrochemical NO reduction by using a solid electrolyte cell. In this study, Electrochemical Reduction by electrochemical cells is proposed to reduce NOx and PM Simultaneously.

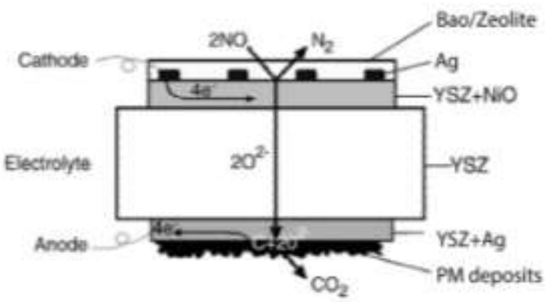


Figure1. Electrochemical NOx reduction Mechanism

3. EXPERIMENTAL SECTION

In this current experimentation, (ZrO_2) (Y_2O_5) YSZ was used as the electrolyte. The YSZ powder with polyvinyl alcohol as a binder is mixed and poured into the module. The mixture is pressed in a hydraulic press to form a square plate of 3 mm thickness and 80×80 mm diameter. The YSZ plate is calcined for 7 hours at 1350°C to produce a solid substrate, which is an electrolyte. YSZ is an ionically conducting material and shows better oxygen ion transfer [7, 8]. The cathode material used NiO and YSZ. The cathode material is made into slurry with polyvinyl alcohol and coated on the YSZ disk. The Anode coating is made by using of Ag paste with YSZ by brush coating over the electrolyte. The fig. 2 shows the Electrochemical cell. Fig. 3 shows the scanning electron microscopy of porous electrolyte and electrodes.

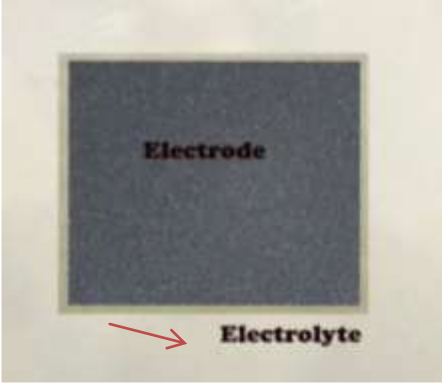
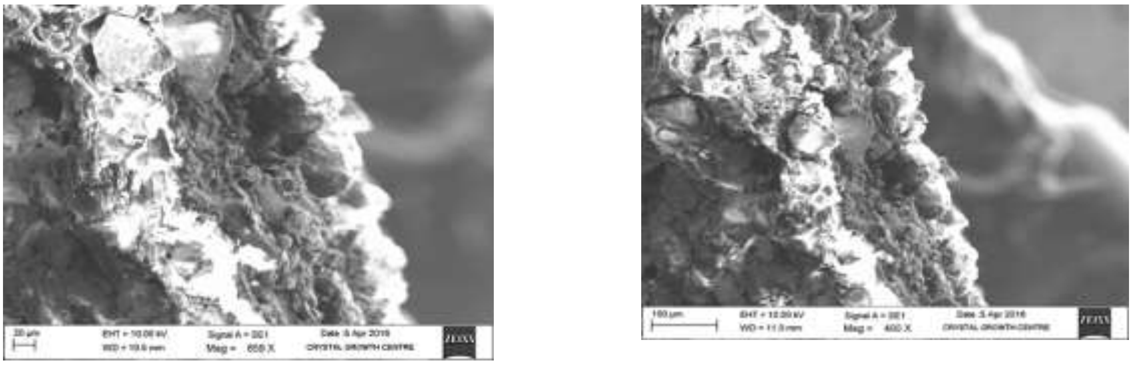


Figure 2. Electrochemical cell



(a) (b)

Figure 3. The Cross Sectional view of manufactured cell (a) Anode and electrolyte (b) Cathode and electrolyte

4. EXPERIMENTAL SET-UP AND TESTING

The experiment was carried out in a single cylinder diesel engine. Fig. 4 shows the experimental set-up of the engine test bench. Initially engine is allowed to run at a constant speed for 10 to 15 minutes at idle load condition until it reaches steady state. The dynamometers were calibrated to avoid loading error. The Electrochemical reactor was fitted to the exhaust pipe with the power supply from the Diesel engine. The NOx emissions were measured by using the Chemiluminescence NOx analyzer for different load conditions.The cross section of the electrochemical reactor device is shown Fig.6. A 12 V battery was used as a power source to activate the electrochemical reactor. The PM emissions were measured by using micro soot sensor and the AVL di gas analyzer was used to measure HC, CO, and CO_2 emissions.

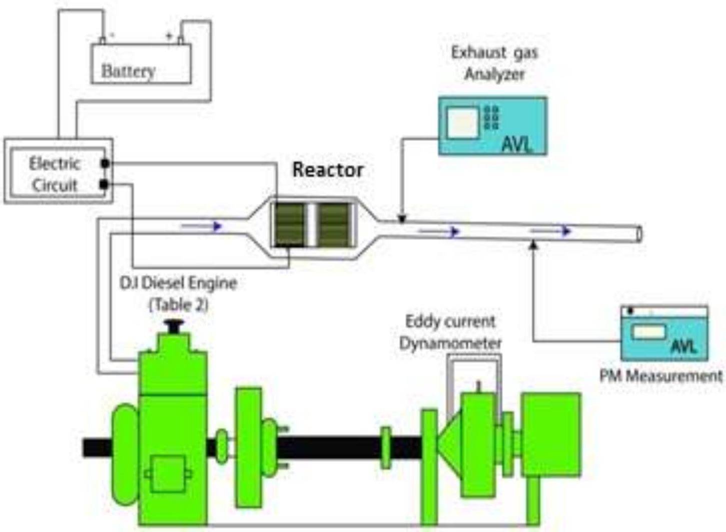


Figure 4. Complete Experimental set-up

5. RESULT AND DISCUSSION

The ENAR cell-1 and cell-2 was fabricated with materials -

Ag+YSZ (anode)/ YSZ (electrolyte)/YSZ+ NiO (cathode)/cu-zeolite (NOx storage)

Ag+YSZ (anode) / YSZ (electrolyte) / YSZ+ NiO (cathode)/BaO (NOx storage)

In Electrochemical cells the decomposition of NOx takes place by passing alternating current. The presence of oxygen concentration in diesel exhausts initiates the reduction of O_2 over the electrolyte and is indicated by the reaction

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (1)$$

The NOx molecules adsorbed on the storage material are decomposed over the electrodes by the reactions.

$$Ni + NO \rightarrow Ni - NO \quad (2)$$

$$2Ni - NO \rightarrow 2NiO + N_2 (3)$$

$$NiO + 2e^- \rightarrow Ni + O (4)$$

The cell-1 had the maximum amount of NO decomposition and Polar like NO and CO_2 has more affinity towards zeolite. . The three dimensional micro structure of the zeolite inter locks the NOx molecule over it. There by supplying electric current to electrode the decomposition of NOx takes place over cathode. In cell-2 BaO was used as a NOx storage material. NOx storage Coating BaO is necessary for the electrochemical reduction of NOx [10]. In this technique, Ba is present over the cathode layer in the form of BaO and reacts with NOx as indicated by reaction R(5)

$$BaO + 2NO_2 + 1/2\ O_2 \rightarrow Ba(NO_3)_2 \ (5)$$

The reduction of NOx is further achieved by decomposition of Ba $(NO_3)_2$ with applied voltage by the reaction R (6)

$$Ba(NO_3)_2 + 2e^- \rightarrow BaO + O^{2-} + 1/2N_2 + NO_2 + O_2 \quad (6)$$

The Electrochemical reactor was tested with two different combinations of Cells. Fig. 5 Shows the Electrochemical cells tested in real exhaust conditions in diesel engine. The Cell-1 showed better NOx reduction over diesel exhaust. The presence of zeolite NOx storage material in the Cell-1 increased the decomposition of NOx up to 85%. In Cell-2 NOx storage material used was BaO. The NOx decomposition rate was slightly lower in Cell-2, which was due to the storage capacity of BaO. It was observed that the NOx storage coating over the cathode layer was necessary to reduce the NOx molecules into N_2. The decomposed oxygen further oxidized the PM emissions.

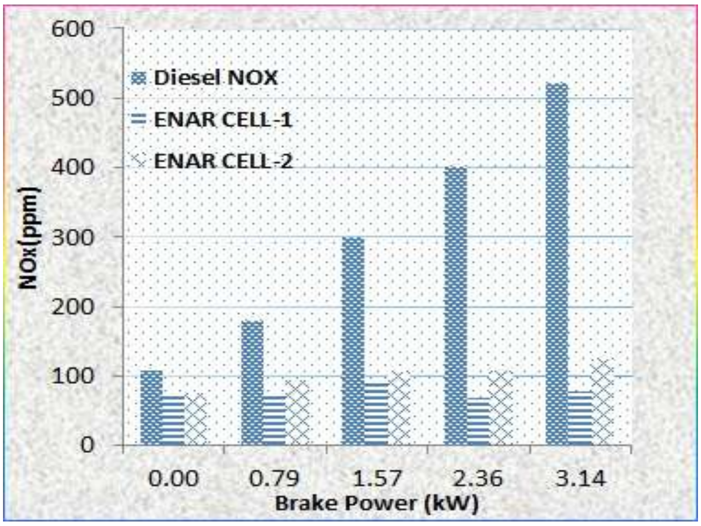


Figure 5. NOx emission with respect to engine Brake Power

The exhaust temperature was measured using thermocouple fixed to the exhaust pipe. The exhaust temperature was an important factor for the activation of the catalyst. The NOx formation increased with the in-cylinder temperature [9]. The exhaust temperature was further increased by increasing the load. The NOx formation also increased with oxygen concentration. Fig. 6.shows the NOx emission with respect to exhaust temperature. It was observed that the activation temperature for the catalytic material fell in the range of 150°C-200°C. The Zeolite decomposition started at Cell-1 even at a lower temperature of 150°C. In Cell- 2 the decomposition started at 150°C because the BaO was not effective at temperatures below 200°C.

The decomposition rate is lesser by using BaO because, the CO_2 in the diesel exhaust reacts with the BaO sites to form the reaction

$$BaO + CO_2 \rightarrow BaCO_3 \quad (7)$$

$$BaCO_3 + 2NO_2 + 1/2O_2 \rightarrow Ba(NO_3)_2 + CO_2 \quad (8)$$

The CO_2 is can be stored in Ba as shown in R(7).The presence of CO_2 in the exhaust produces fast production of BaCO3.The $BaCO_3$ is finally converted in to $Ba(NO_3)_2 + CO_2$, as shown in R(8) .The reaction rate of R(8) is slower than R(7) . Therefore CO_2 is the exhaust will reduce the NOx storage rate with BaO there by reduces the decomposition rate of NOx with respect to cell-2.

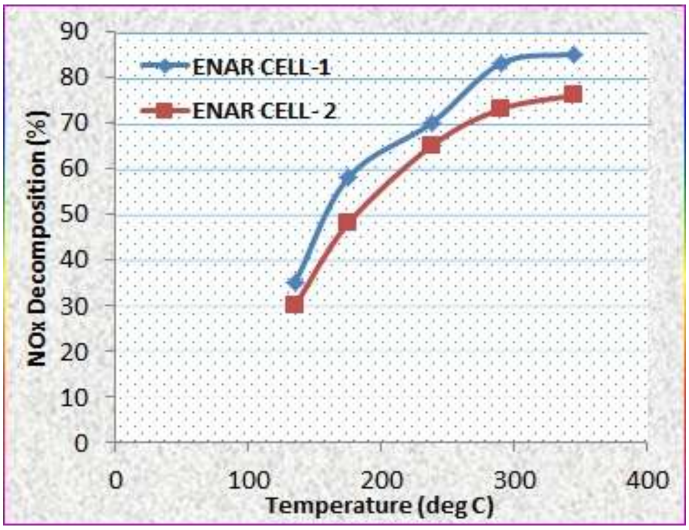


Figure 6. NOx emission with respect to exhaust gas temperature

5.1 Simultaneous Reductions

The cells were tested for simultaneous reduction of PM and NOx in the diesel exhaust and they were tested in a single cylinder diesel engine in variable load conditions. Fig. 7.shows the PM oxidation on Electrochemical Cells. The voltage applied to the cell initiated the reduction of NO_X and PM oxidation.

$$2NO+4e^{-} \rightarrow N2+2O^{2-}$$

$$C+2O^{2-} \rightarrow CO_2+ 4e^{-}$$

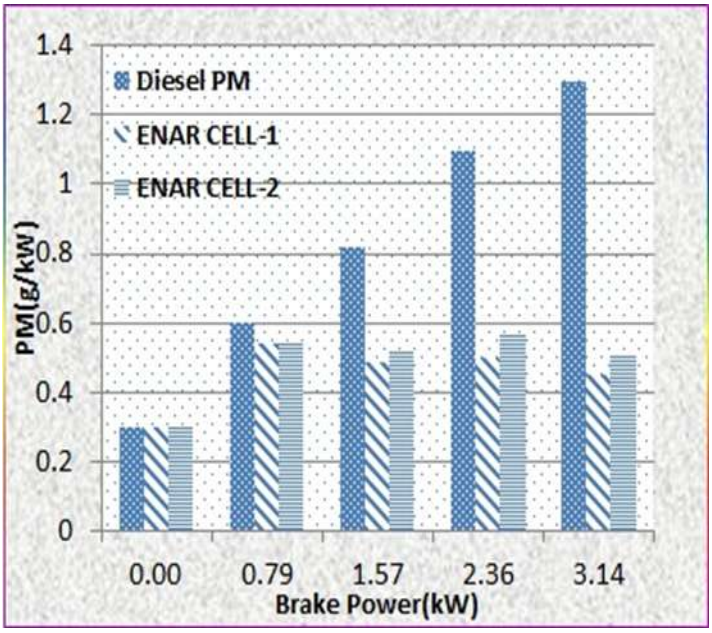


Figure 7. Particulate matter emission with respect to engine Brake power

By applying a current of 0-15 V, PM oxidation and reduction was achieved more than 65%. The PM oxidation increased with Cell-1 because of the maximum NOx storage capacity of zeolite. The decomposition of NOx into N_2 and O_2 increased and the decomposed oxygen ions from the electrolyte oxidized the PM deposits effectively on the anode layers.

Conclusion

This is a vital technique to reduce diesel engine NOx emissions. The electrochemical NOx reduction for the real exhaust condition was tested. In this technology by passing electric current simultaneous reduction of NOx and PM can be achieved. In this method, 80 % reduction of NOx and 65% of PM is achieved at the effective temperature of 350°C. The flow rate of exhaust is constant and the temperature varies with increasing loads. It is observed from the results that at 250-350ºC are the efficient range for theelectrochemical cells for the maximum NO_x decomposition. Because YSZ is an ionically conducting ceramic, this works efficiently when the surface is heated above 200ºC.It was observed that by coating the NOx storage material, the NOx reduction efficiency increased drastically. The results shows zeolite has good NOx adsorption capacity even at low temperatures 150°C. Low- temperature operation (150°C) was also achieved by the development of this technique. It is considered that proposed result of emission reduction and low temperature activation can be most suitable technique for light duty vehicles.

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